

---

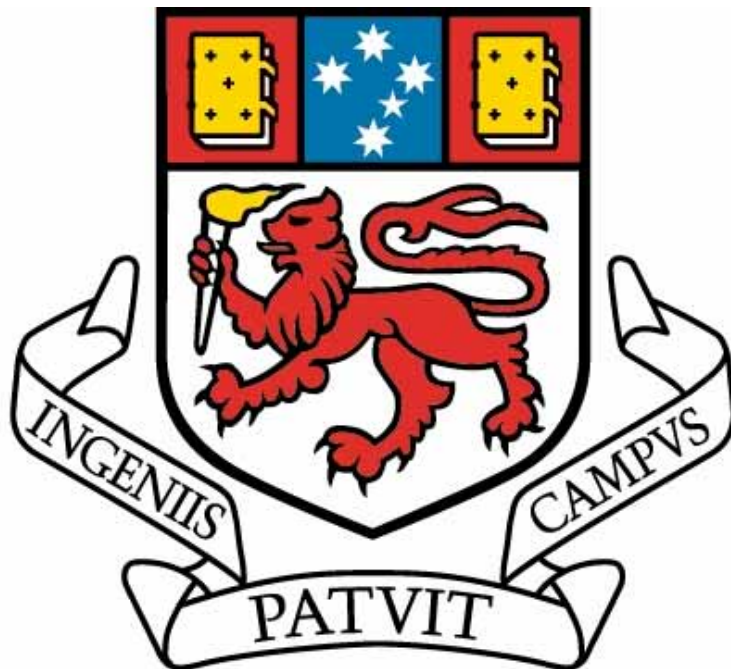
**A new methodology for the study of the magmatic-  
hydrothermal transition in felsic magmas: applications  
to barren and mineralised systems**

---

by

**Paul Davidson**

B.Sc Hons (University of Tasmania)



Submitted in fulfilment of the requirements for the degree  
of Doctor of Philosophy

University of Tasmania  
Australia

May, 2004



Rio Blanco, Chile, in the background deformed Abinico Formation (Los Pelambres Formation) is overlain by the Farellones Formation. In the foreground is the tailings dam in the Rio Blanco Valley. Photograph courtesy of Dr. Peter Hollings

---

## Statement

This thesis contains no material which has been accepted for the award of any other degree or diploma in any tertiary institution and, to the best of my knowledge and belief, contains no copy or paraphrase of material previously published or written by any other person, except where due reference is made in the text of the thesis.

Date:            /            /

Signature:

---

## Authority of Access

This thesis may be made available for loan and limited copying in accordance with the Copyright Act 1968.

---

## Acknowledgments

No man is an island, and no PhD. is ever the sole work of any one person. I gratefully acknowledge the unstinting help, and encouragement, that I have received over the years during which I have worked towards fulfilment of this project.

First and foremost I thank my family, without their love and support I could not have even begun such a project. To my parents, Thomas and Dorothea, my sisters, Sheena, Joy, Kathleen, and Susan, and my tribe of nephews and nieces, my thanks. I returned to higher education late in life, and could only contemplate doing so knowing that I had the complete and unquestioning support of everyone that is important to me. A leap in the dark is so much easier knowing that you began from a safe place, and can always return.

Particular thanks must go to my thesis supervisors, Dr. Dima Kamenetsky, and Professor Tony Crawford. Any PhD candidate knows that selection of a supervisor can be a make- or break decision, and it has been my good fortune to have chosen the best supervisors I could have hoped for. Nothing has been too much trouble, and their doors have always been open. Dima has been unstinting in introducing me the mysteries of melt inclusion techniques, and exceptionally patient with his own “sorcerers apprentice”.

One fundamental problem for anyone proposing a melt inclusion study is finding melt inclusions to study. My thanks to Dr. David Cooke and the GODS team, particularly Peter Frikken and Peter Hollings, who provided the Río Blanco samples and their geological overview. Likewise, my thanks to Dr. Sharon Allen for the Okataina samples. Both sets of samples provided many insights into the processes of volatile phase exsolution, and a synthesis from both provided many more.

Particular thanks are also due to Maya Kamenetsky and Simon Stephens for their lapidary work on my behalf. Skilful lapidary work is a day-to-day requirement in melt inclusion studies, and Maya and Simon have each made important contributions to my work. Thanks also to Leonid Danyushevsky for his invaluable assistance with the LA-ICPMS analyses for this thesis. My thanks to all of the technical staff, my name is on the cover of this thesis, but you will see your work in every analysis, every thin section, and every hour I was at my desk.

More generally I must thank all of the teaching and research staff of CODES and the Earth Science department of the University of Tasmania. From my first days as an undergraduate student no doors have been closed to me, and there have always been specialists in any number of fields whose knowledge and experience has been there for

the asking. I must particularly thank Professor Ross Large, as head of CODES Ross has the task of keeping the doors open and everything ticking over. Each researcher knows that we are only able to do the things that so interest us, because we have a roof over our heads, and someone else to deal with the world beyond our doors.

I must acknowledge a debt of gratitude to everyone that has made my time at University so enjoyable. Albert Einstein once said that the best job in the world for a physicist would be as a lighthouse keeper, but it would not be so for a geologist. The constant, open, and unrestricted interactions between staff, students, and external researchers are the great strength of CODES. We all gain, personally, and professionally, from the strength of our close knit community. I am not demonstrative by nature, but my candidature has been one of the best and most fulfilling periods of my life, and I have everyone at the University of Tasmania, and CODES in particular to thank.

My acknowledgments must also extend beyond the CODES community, microanalytical techniques have driven melt inclusion studies, and this thesis has been enriched by the work of several people. Electron microprobe analyses, Dr David Steele, of the Central Science Laboratory, University of Tasmania, Hobart. Laser Raman analyses, Dr Terry Mernagh, from the Minerals Division, Geoscience Australia, Canberra, and PIXE microprobe analyses Dr. Chris Ryan, and Esme van Achterbergh, CSIRO Exploration and Mining, North Ryde, Sydney, and LA-ICPMS analyses from Dr. Steve Eggins of the Australian National University, Canberra.

To one and all, my thanks.

---

# **A new methodology for the study of the magmatic-hydrothermal transition in felsic magmas: applications to barren and mineralised systems**

---

## **Abstract**

This study aims to develop a robust research methodology to examine the evolution of magmatic volatile phases during the cooling of felsic magmas via detailed melt- and fluid-inclusion studies, in particular the investigation of inclusions originally containing both melt and aqueous fluid. Then, using these techniques I will examine fluid immiscibility processes in two felsic magmatic systems, one mineralised, the other barren. In particular, I address the constraints on the exsolution of magmatic vapour and aqueous liquids, and how it is manifested in quartz-hosted inclusions, as well as the nature and composition of the exsolved phases. In developing a research philosophy two factors need to be paramount, it needs to be as widely applicable as possible, and the limitations need to be recognised and explored. Thus, the results deriving from these techniques may provide a test of the methodology.

The thesis is based on two case studies, Río Blanco (Chile) and Okataina (New Zealand). The first case study involves sub-volcanic intrusives and associated extrusives from the La Copa Rhyolite, and intrusives from the Don Luis Porphyry, two post-ore rhyolitic suites from the Los Bronces-Río Blanco Porphyry Cu-Mo deposit. The second case study involves rhyolitic lavas (< 65 Ka) from the Okataina Volcanic Centre in the Taupo Volcanic Zone in New Zealand. This study is not intended to examine the geology of these systems, but rather to use them as examples of felsic systems, in diverse tectonic settings. Both as test cases for developing robust research techniques and for any information that they can provide regarding late-stage magmatic processes, particularly volatile phase exsolution, and the role of melt/fluid and liquid/vapour immiscibility.

At Río Blanco, the melt inclusion populations consist predominantly of glass inclusions and coexisting dark, inhomogeneous crystalline silicate melt inclusions (CSMI's). An important discovery from this study is the recognition that CSMI's trap volatile-rich melt, probably identical to the melt trapped as glass inclusions, and are crystallised, not “devitrified” or the product of post-magmatic alteration. Heating experiments demonstrate that both the glass and CSMI's from Río Blanco have decrepitated and degassed post-trapping, notwithstanding the apparent lack of petrographic indicators of degassing in the glass inclusions. This coexistence appears to

be a common occurrence; however, its significance seems to have been overlooked in a number of previous studies.

From an initial volatile-rich melt, aqueous volatile phases (dominantly vapour) exsolved, forming bubbly magmatic emulsions. Inherently, magmatic emulsions are metastable, and disrupt into discrete melt and vapour phases. The vapour-rich phases separated from the melt and escaped, cooling, condensing, and mixing as they did so. Río Blanco melt inclusions and fluid inclusions trapped all of these phases, in various combinations, both demonstrating the process in fine detail, and sampling the phase compositions. Analysis of the phases demonstrates partitioning of metals (Cu, Zn, and possibly Pb) into the vapour phase, its transport out of some of the magma bodies, and implies concentration by mixing and condensing to form metal-rich hypersaline fluid inclusions in the carapace of the Don Luis Porphyry.

The Okataina case study provided an invaluable counterpoint to Río Blanco. Phenocryst crystallisation pressures were supercritical, although the evidence suggests that volatile phase exsolution (VPE) occurred post- rather than pre-trapping, so that trapped magmatic emulsions are not observed. Okataina also contains coexisting CSMI's and glass inclusions, although many of the samples contains a complex array of partly crystalline silicate melt inclusions. Importantly for this study, many of the inclusions do homogenise during experimental heating, indicating that decrepitation and degassing were not as pronounced as at Río Blanco. Heating experiments showed that despite coexisting CSMI's and glass inclusions, there was only a single melt trapped. This provides evidence of the post-trapping behaviour of melt inclusions, lacking at Río Blanco. Although pre-trapping VPE did not occur to a large degree, post-trapping VPE did. Inclusions in which exsolution of an aqueous volatile phase has occurred provide a measure and sample of the amounts of fluids that were exsolved from a known quantity of melt, and may provide a method of determining the actual amounts of hydrothermal fluids that a magma body may exsolve.

In evaluating these results some inevitable limitations of the techniques have been uncovered, particularly those relating to the vagaries of melt inclusion formation and preservation, and these have been evaluated. However, qualitative, and to some extent quantitative results have been produced, some of which have been published in research journals. Together, the case studies demonstrate and sample the fine detail of the exsolution of volatile-rich phases from silicate melts, their escape from those melts, and eventual cooling and condensing to form the kinds of hypersaline hydrothermal fluids found as fluid inclusions in ore-bodies. Further, they provide insights into common post-trapping behaviours of melt inclusions, some aspects of which appear to have been misinterpreted in some published melt inclusion studies.

# Table of Contents

Statement .....	II
Acknowledgement .....	III
Abstract .....	V
Table of Contents .....	VII
Index of figures .....	XIV
Index of tables .....	XVIII
Glossary .....	XX
 Chapter 1 .....	 1
Statement of the problem.....	1
Rationale for this study.....	2
The significance of volatile-rich phase immiscibility .....	2
The significance of volatiles in natural silicate melts .....	3
The significance of immiscible aqueous fluid phases .....	5
Methodological significance of this study.....	5
Aims of this study.....	6
Why study melt inclusions?.....	7
Structure of this thesis .....	8
Chapter 2: Melt inclusion study techniques .....	9
Introduction .....	9
Sample preparation .....	9
Petrographic examination and description.....	10
Compromised inclusions .....	11
Homogenisation.....	11
Introduction .....	11
Heating stage homogenisation .....	12
Bulk homogenisation .....	13
Potential problems with homogenisation .....	13
Inclusion leakage .....	13
Experimentally induced diffusive H <sub>2</sub> O loss.....	14
Fracturing of host during homogenisation .....	14
Effects that cannot be reversed by homogenisation .....	15
Diffusive re-equilibration with the host.....	15
Inhomogeneous trapping.....	15

Chapter 3: Analytical Techniques .....	16
Introduction.....	16
Electron Microprobe.....	16
Electron microscopy .....	17
SEM EDS .....	17
Laser Raman .....	17
LA-ICPMS .....	18
PIXE .....	19
Section 2 Case Studies .....	20
Río Blanco Case Study.....	20
Chapter 4: Regional & Local geology.....	20
Introduction.....	20
Tectonics .....	22
Geology .....	23
Late Porphyries .....	24
The La Copa Volcanic Complex.....	26
The Don Luis Porphyry .....	26
Mineralisation .....	26
Sample descriptions.....	27
Don Luis Porphyry .....	27
La Copa Volcanic Complex .....	27
Intrusive Samples.....	27
Extrusive Samples.....	28
Samples CA30 & CA31 .....	28
Sample CA32.....	28
Sample CA33.....	28
Chapter 5: Description of Magmatic Inclusions.....	30
Introduction.....	30
Occurrence of inclusions.....	30
Inclusion types .....	35
Glass inclusions.....	35
Crystallised glass inclusions.....	41
Crystalline silicate melt inclusions .....	48
Characteristics .....	48
Decrepitation features .....	49
Microphenocryst inclusions.....	49



Feldspar .....	58
Other minerals .....	58
Significant features of microphenocrysts .....	59
Fluid inclusions.....	59
La Copa Volcanic Complex .....	59
Primary fluid inclusions .....	59
Vapour-rich fluid inclusions .....	59
Liquid-rich fluid inclusions .....	66
Primary /pseudosecondary fluid inclusions .....	66
Secondary fluid inclusions.....	67
Don Luis Porphyry .....	67
High salinity fluid inclusions .....	67
Low-salinity fluid inclusions .....	72
Fluid inclusion summary .....	72
Composite inclusions.....	73
Composites of glass and crystallised silicate melt .....	73
Composites of glass and primary magmatic aqueous fluids .....	80
General characteristics of composite inclusions.....	80
Chapter 6: Analytical Results.....	81
Introduction.....	81
Whole Rock Analyses .....	81
Glass inclusions .....	85
Microprobe Analyses.....	85
Comparison with whole rock composition .....	85
Comparison between samples.....	87
Crystalline silicate melt inclusions .....	87
Composite inclusions .....	107
Composites of glass and crystalline silicates .....	107
Composites of glass and primary magmatic fluid .....	112
Fluid Inclusions.....	113
Primary magmatic fluid inclusions .....	113
Hypersaline fluid inclusions .....	113
Summary.....	132
Chapter 7: Experimental Results .....	133
Introduction.....	133
Homogenisation experiments.....	133
Glass inclusions .....	133

- Individual heating experiments.....	133
Introduction .....	133
Results .....	134
Crystallised silicate melt inclusions .....	135
Río Blanco inclusions .....	135
- Individual heating experiments .....	135
- Bulk heating experiments .....	135
Introduction .....	135
Results .....	140
Don Luis Porphyry inclusions.....	146
- Bulk heating experiments .....	146
Introduction .....	146
Results .....	146
Microthermometry .....	147
Introduction .....	147
Don Luis Porphyry .....	152
Multi-phase inclusions .....	152
2-phase inclusions .....	154
Summary of the microthermometry .....	155
Composite inclusions of glass+primary magmatic fluid .....	156
Conclusions from the analytical and experimental work.....	160
Current whole rock composition .....	160
Glass inclusions.....	161
Crystalline silicate melt inclusions .....	161
Composite inclusions .....	162
Glass + Crystalline silicates .....	162
Glass+primary magmatic fluids .....	162
Fluid Inclusions .....	162
Hypersaline, magmatic mineral-bearing inclusions .....	162
Hypersaline fluid inclusions.....	162
Low salinity fluid inclusions .....	163
Chapter 8: Discussion and Conclusions .....	164
Discussion .....	164
Introduction.....	164
Melts represented by Río Blanco melt inclusions.....	164
Crystalline silicate melt inclusions .....	164

Glass inclusions .....	166
Decrepitation and degassing in Río Blanco melt inclusions .....	166
Aqueous magmatic fluid phase .....	167
Co-existence of silicate melts and aqueous magmatic fluids .....	167
Immiscibility of silicate melts and aqueous magmatic fluids .....	168
Physical characteristics of volatile phase exsolution .....	169
The exsolution of aqueous fluids at Río Blanco .....	169
A proposed mechanism .....	169
The derivation of aqueous fluids in the Don Luis Porphyry .....	134
Compositional consequences of volatile phase exsolution .....	176
Fractionation of metals from the Río Blanco magma .....	178
Fractionation of metals in the Río Blanco fluid phases .....	181
Consequences for metallogenesis .....	184
Conclusions .....	185
Okataina Case Study .....	187
Chapter 9: Local and Regional Geology .....	187
Introduction .....	187
Regional Geology of the Taupo Volcanic Zone .....	187
Introduction .....	187
Tectonics and Geology .....	190
The Okataina Volcanic Centre .....	192
Introduction .....	192
Geological history of the Okataina Volcanic Centre .....	194
Rhyolite domes from the Okataina Volcanic Centre .....	194
Petrology of the Okataina rhyolites .....	195
Sample selection and descriptions .....	196
Chapter 10: Inclusion Descriptions .....	198
Introduction .....	198
Patterns of inclusion occurrence .....	198
Inclusion descriptions .....	198
Glass inclusions .....	198
Crystal-rich and granular-textured glass inclusions .....	204
Crystalline silicate melt inclusions .....	215
Microphenocryst inclusions .....	228
Aqueous globules in Okataina inclusions .....	228
Chapter 11: Experimental Results .....	229

Introduction.....	229
Homogenisation of Okataina inclusions.....	230
Large-bubble glass inclusions.....	234
Small-bubble clear glass inclusions.....	234
Crystal-rich and granular-textured glass inclusions.....	235
Crystal-rich glass inclusions.....	242
Experimentally induced in-situ immiscibility.....	242
Fluid inclusion microthermometry.....	243
Summary of heating experiments.....	243
Chapter 12: Analytical Results.....	247
Sample analyses.....	247
Inclusion Analysis.....	251
Introduction.....	251
Detailed analytical studies.....	255
NZL1g and NZL2d.....	256
Evidence of degassing.....	259
NZL16b and NZL27b.....	267
Comparisons between NZL1g and NZL2d, and NZL16b and NZL27b....	270
Experimentally induced in-situ immiscibility.....	271
Microthermometry.....	274
Summary of analytical results.....	275
Chapter 13: Discussion and Conclusions.....	277
Melts represented by Okataina melt inclusions.....	277
Decrepitation of crystalline silicate melt inclusions.....	278
Implications of degassing.....	278
Inferences from homogenisation temperatures.....	279
Did aqueous fluids coexist with silicate melt at Okataina?.....	279
In-situ immiscibility.....	280
Implications of in-situ immiscibility.....	282
Conclusions.....	283
Chapter 14: Methodological implications of this study.....	285
Introduction.....	285
Coexistence of volatile-poor and volatile-rich melts.....	285
Inclusions that cannot be homogenised.....	286

Inclusions that can be homogenised .....	287
Summary .....	288
Chapter 15: Discussion and Conclusions .....	289
Discussion .....	289
Introduction.....	289
Immiscibility in the Río Blanco magmas.....	289
Melt/melt immiscibility .....	289
Melt/vapour immiscibility, via magmatic emulsions .....	294
Exsolution of aqueous phases .....	295
The composition of exsolved primary magmatic fluids .....	295
When did exsolution occur?.....	299
VPE at Río Blanco and Okataina: summary models.....	299
Río Blanco.....	302
Okataina .....	303
Cooling magmas and the derivation of hydrothermal fluids.....	304
Conclusions .....	305
Exsolution of volatile phases .....	305
Melts .....	306
Magmatic emulsions.....	306
Primary magmatic fluids.....	307
References .....	308
 Appendix A Microprobe data.....	 322
Appendix B Publications.....	336

# Index of Figures

## Río Blanco case study

### Chapter 4: Local and Regional Geology

4-1 Map of South America, with contours of the top of the Benioff Zone .....	21
4-2 Lithographic cross-section through the Chilean Flat-Slab Segment.....	22
4-3 Simplified geological map of the Los Bronces to Río Blanco deposit .....	25

### Chapter 5: Inclusion descriptions

5-1 to 5-6 Photomicrographs of magmatic inclusions .....	33
5-7 to 5-12 Photomicrographs of magmatic inclusions .....	37
5-13 to 5-19 Photomicrographs of magmatic inclusions .....	39
5-18a Histogram of bubble-fractions for Río Blanco melt inclusions .....	40
5-18b Graph of bubble-fractions for Río Blanco melt inclusions .....	40
5-20 to 5-24 Photomicrographs of magmatic inclusions .....	43
5-25 to 5-30 Photomicrographs of magmatic inclusions .....	45
5-31 to 5-34 Photomicrographs of magmatic inclusions .....	47
5-35 to 5-37 Electron photomicrographs of magmatic inclusions .....	51
5-38 to 5-40 Electron photomicrographs of magmatic inclusions .....	53
5-41 to 5-45 Photomicrographs of magmatic inclusions .....	55
5-46 to 5-50 Photomicrographs of magmatic inclusions .....	57
5-51 to 5-56 Photomicrographs of magmatic inclusions .....	61
5-57 to 5-60 Photomicrographs of magmatic inclusions .....	63
5-61 to 5-65 Photomicrographs of magmatic inclusions .....	65
5-66 to 5-71 Photomicrographs of magmatic inclusions .....	69
5-72 to 5-77 Photomicrographs of magmatic inclusions .....	71
5-78 to 5-82 Photomicrographs of magmatic inclusions .....	75
5-83 to 5-87 Photomicrographs of magmatic inclusions .....	77
5-88 to 5-92 Photomicrographs of magmatic inclusions .....	79

### Chapter 6: Analytical Results

6-1 Plot of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ , Río Blanco whole-rock analyses recalculated to 100%....	84
6-2 Plot of $\text{K}_2\text{O}$ vs $\text{SiO}_2$ , whole-rock analyses recalculated to 100% .....	84
6-3 Plot of Total wt% vs $\text{SiO}_2$ , for Río Blanco glass inclusions .....	86
6-4 Plot of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ , for glass inclusions .....	86
6-5 Plot of Total wt% vs $\text{SiO}_2$ , for glass inclusions, recalculated to 100 wt% .....	88
6-4 Plot of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ , for Río glass inclusions recalculated to 100 wt% .....	88
6-7 Table of microprobe analyses, and photomicrograph showing locations.....	89

6-8 Photomicrograph of CSMI with associated Laser Raman spectra .....	93
6-9 Photomicrograph of CSMI with associated Laser Raman spectra .....	93
6-10 PIXE element maps for BM36a, a CSMI .....	95
6-11 PIXE element maps for BM36b, a CSMI .....	97
6-12 PIXE element maps for BM18, a CSMI .....	97
6-13 PIXE element maps for BM34, a CSMI .....	99
6-14 PIXE element maps for BM31, a vapour-rich CSMI .....	99
6-15 PIXE element maps for BM35, a vapour-rich CSMI .....	101
6-16 PIXE element maps for BM32, a vapour-rich CSMI .....	101
6-17 PIXE element maps for BM36c, a vapour-rich CSMI .....	103
6-18 PIXE element maps for BM33, a vapour-rich CSMI .....	103
6-19 PIXE element maps for BM19, a hypersaline fluid-rich CSMI .....	105
6-20 LA-ICPMS spectra of a CSMI .....	105
6-21 PIXE element maps for BM41, a composite inclusion .....	109
6-22 PIXE element maps for BM42a, a composite inclusion .....	109
6-23 PIXE element maps for BM45a, a composite inclusion .....	111
6-24 PIXE element maps for PD1, a composite inclusion .....	111
6-25 PIXE element maps for BM28, a liquid-globule composite inclusion.....	115
6-26 PIXE element maps for BM48, an emulsion inclusion .....	115
6-27 PIXE element maps for BM47, an emulsion inclusion .....	117
6-28 PIXE element maps for BM43, a magmatic vapour inclusion .....	117
6-29 to 6-34 Photomicrographs of magmatic inclusions.....	119
6-35 PIXE element maps for BM15, a hypersaline fluid inclusion .....	121
6-36 PIXE element maps for BM15b, a hypersaline fluid inclusion .....	121
6-37 PIXE element maps for BM16b, a hypersaline fluid inclusion .....	123
6-38 PIXE element maps for BM17, a hypersaline fluid inclusion .....	123
6-39 PIXE element maps for BM21a, a hypersaline fluid inclusion .....	125
6-40 PIXE element maps for BM21b, a hypersaline fluid inclusion .....	125
6-41 PIXE element maps for BM7b, a hypersaline fluid inclusion .....	127
6-42 PIXE element maps for BM7a, a hypersaline fluid inclusion .....	127
6-43 PIXE element maps for BM16, a hypersaline fluid inclusion .....	128
<b>Chapter 7: Experimental Results</b>	
7-1 Sequence of photomicrographs showing progress of a heating experiment .....	137
7-2 Ditto, for a small CSMI .....	139
7-3 Ditto, for a large CSMI .....	139
7-4 to 7-7 Photomicrographs of magmatic inclusions .....	143

7-8 Plot of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ , bulk heating results, sample CA31.....	141
7-9 Plot of Total wt% vs $\text{SiO}_2$ , bulk heating results, sample CA31 .....	141
7-10 Plot of $\text{K}_2\text{O}$ vs $\text{Na}_2\text{O}$ , bulk heating results, sample CA31.....	144
7-11 Plot of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ , bulk heating results, sample CA33 .....	144
7-12 Plot of $\text{K}_2\text{O}$ vs $\text{Na}_2\text{O}$ , bulk heating results, sample CA33.....	145
7-13 to 7-17 Photomicrographs of magmatic inclusions .....	149
7-18 PIXE element maps for PD2, a globule-rich, partly homogenised CSMI .....	151
7-19 PIXE element maps for PD3, a globule-rich, partly homogenised CSMI.....	151
7-20 Histograms of $T_h$ 's of Don Luis Porphyry fluid inclusions.....	153
7-21 Sequence of photomicrographs showing metastability .....	157
7-22 Sequence of photomicrographs showing metastability .....	158
7-23 Histograms of Don Luis Porphyry freezing point depression temperatures .....	160

## **Chapter 8: Río Blanco; Discussion and Conclusions**

8-1 to 8-5 Photomicrographs of magmatic inclusions .....	173
8-6 to 8-7 Electron photomicrographs of magmatic inclusions .....	175
8-8 Inter-element ratios of Río Blanco CSMI's vs apparent silicate content .....	179
8-9 Inter-element ratios of Río Blanco CSMI's vs K .....	180
8-10 Inter-element ratios of Río Blanco CSMI's vs K/Mn .....	180
8-11 Cu vs K/Mn for Río Blanco CSMI's .....	182
8-12 Fe vs K/Mn for Río Blanco CSMI's .....	182
8-13 Pb vs K/Mn for Río Blanco CSMI's .....	183
8-14 Cu vs Ca/Mn for Río Blanco CSMI's .....	183

## **Okataina Case Study**

### **Chapter 9: Local and Regional Geology**

9-1 Map of the North Island, New Zealand, showing subduction features .....	188
9-2 Map of the TVZ, showing structural margins of all caldera structures.....	189
9-3 Combined geological-geophysical cross-section of the North Island .....	191
9-4 Map of the Okataina caldera complex.....	193

### **Chapter 10: Inclusion descriptions**

10-1 to 10-5 Photomicrographs of magmatic inclusions .....	201
10-6 to 10-11 Photomicrographs of magmatic inclusions .....	201
10-12 to 10-14 Electron photomicrographs of magmatic inclusions .....	207
10-15 to 10-20 Photomicrographs of magmatic inclusions .....	209
10-21 to 10-24 Photomicrographs of magmatic inclusions .....	211
10-25 to 10-28 Photomicrographs of magmatic inclusions .....	213



10-29 Electron photomicrographs of magmatic inclusions .....	217
10-30 to 10-31 Electron photomicrographs of magmatic inclusions .....	219
10-32 to 10-37 Photomicrographs of magmatic inclusions .....	221
10-39 to 10-39 Electron photomicrographs of magmatic inclusions .....	223
10-40 to 10-45 Photomicrographs of magmatic inclusions .....	225
10-46 to 10-51 Photomicrographs of magmatic inclusions .....	227
<b>Chapter 11: Experimental Results</b>	
11-1 to 11-5 Photomicrographs of magmatic inclusions .....	233
11-6 Sequence of photomicrographs showing progress of a heating experiment .....	237
11-7 Sequence of photomicrographs showing progress of a heating experiment .....	238
11-8 to 11-10 Photomicrographs of magmatic inclusions .....	245
<b>Chapter 12: Analytical Results</b>	
12-1 Photomicrograph of thin section of sample NZL16b .....	247
12-2a Plot of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ , matrix glasses and whole rock analyses .....	250
12-2b Plot of $\text{P}_2\text{O}_5$ vs $\text{SiO}_2$ , matrix glasses and whole rock analyses .....	250
12-3 Plot of Total wt% vs $\text{SiO}_2$ for the 8 baseline samples .....	251
12-4 Inter-element plots of the 8 baseline samples .....	253
12-5 Inter-element plots of the 8 baseline samples, recalculated to 100 wt% .....	254
12-10a Plot of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ , matrix and inclusion glasses .....	257
12-10b Plot of $\text{K}_2\text{O}$ vs $\text{Na}_2\text{O}$ , matrix and inclusion glasses .....	257
12-6 to 12-9 Photomicrographs of magmatic inclusions .....	261
12-11a Plot of Total wt% vs $\text{SiO}_2$ , heated and unheated inclusions, NZL 1g .....	258
12-11b Plot of Total wt% vs $\text{SiO}_2$ , heated and unheated inclusions, NZL 2d .....	258
12-12a Plot of Cl vs $\text{SiO}_2$ , heated and unheated inclusions, NZL 1g .....	262
12-12b Plot of Cl vs $\text{SiO}_2$ , heated and unheated inclusions, NZL 2d .....	262
12-13 Plot of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ , recalculated to 100 wt%, NZL 1g and NZL 2d .....	263
12-14 Plot of $\text{K}_2\text{O}$ vs $\text{Na}_2\text{O}$ , recalculated to 100 wt%, NZL 1g and NZL 2d .....	263
12-15 Plot of CaO vs MgO, recalculated to 100 wt%, NZL 1g and NZL 2d .....	264
12-16 Composition change between homogenised CR&GT and glass inclusions .....	265
12-17 Ditto, as percentages .....	265
12-18 Results of mass balance calculation .....	266
12-19 Spidergram of Okataina melt inclusions, normalised to primitive mantle .....	269
12-20 Plot of Total wt% vs $\text{SiO}_2$ , unheated inclusions, NZL16b and NZL 27b .....	269
12-21 Plot of $\text{K}_2\text{O}$ vs $\text{Na}_2\text{O}$ , unheated inclusions, NZL16b and NZL 27b .....	270
12-22 PIXE element maps of inclusions containing heating experiment globules .....	272
12-23 PIXE element maps of decrepitation-related fluid inclusions .....	276

## **Chapter 15: Discussion and Conclusions**

15-1 General solvus diagram for silicate melts .....	291
15-2 General solvus diagram for silicate melts .....	291
15-3 Solvus diagram from Davidson and Kamenetsky (2001) .....	293
15-4 to 15-9 Photomicrographs of magmatic inclusions .....	297
15-10 Immiscibility solvus diagram representing conditions at Río Blanco .....	301
15-11 Immiscibility solvus diagram representing conditions at Okataina .....	301
15-12 Photomicrograph of a possible magmatic emulsion melt inclusion .....	303

## **Index of Tables**

### ***Río Blanco case study***

#### **Chapter 6: Analytical Results**

6-1 Whole rock XRF analyses for all Río Blanco samples .....	82
6-2 Whole rock XRF analyses recalculated to 100 wt% .....	83
6-3 PIXE microprobe analyses of fluid inclusions from the Don Luis Porphyry .....	106
6-4 Electron microprobe analyses of composite inclusions .....	107
6-5 LA-ICPMS analysis of Don Luis Porphyry fluid inclusions, in ppm .....	130
6-6 LA-ICPMS analysis of Don Luis Porphyry fluid inclusions, in percentages .....	131

#### **Chapter 7: Experimental Results**

7-1 Summary of $T_h$ 's of Don Luis Porphyry fluid inclusions .....	152
---	-----

#### **Chapter 8: Río Blanco; Discussion and Conclusions**

8-1 PIXE analyses of Río Blanco CSMI's, ranked by vapour content .....	178
--	-----

### ***Okataina Case Study***

#### **Chapter 10: Inclusion descriptions**

10-1 Table of sample locations and melt inclusion populations .....	199
---	-----

#### **Chapter 12: Analytical Results**

12-1 Analyses of samples from the Tarawera eruptive centre .....	249
12-2 Analyses of samples from the Haroharo centre .....	249
12-3 Analyses of melt inclusions (average and $1\sigma$ ) .....	255
12-4 Spot microprobe analyses of crystal-rich glass inclusions .....	256
12-5 Mass balance calculations .....	267
12-6 Trace and rare-earth element concentrations for matrix and inclusion glass .....	268
12-7 PIXE analyses of heating experiment hypersaline globules .....	271
12-8 Compositions for heated and unheated inclusions, and matrix glasses .....	273

12-9 Mass balance calculations for heating experiment glass inclusions.....	273
12-10 PIXE analyses of decrepitation-related fluid inclusions .....	275

## **Index of Diagrams**

### **Chapter 5: Inclusion descriptions**

5-1 Diagrammatic representation of melt inclusion distribututions at Río Blanco .....	31
---	----

# Glossary

Although the first studies of magmatic inclusions are found in the work of Sorby, (1858), recent advances in microanalytical techniques have made their quantitative study possible. Consequently, magmatic inclusion studies are a relatively new field, and as a result there is an ongoing problem of terminology. One consistent observation in magmatic inclusion studies is that typically, each suite contains numbers of inclusions, sufficiently similar to form several natural categories, although these categories vary from suite to suite. The normal solution to this problem of description is to invent a terminology of inclusion types for a particular study (type-1, type-2, type A, type B etc.). There being no requirement that the characteristics of a “type 1” inclusion in one study will correspond to a “type 1” inclusion from a different study, or a different author.

For the purpose of this thesis I have listed, and defined some of the terms I intend to use, some are conventional, and others have, of necessity, been created for this study.

- **Magmatic inclusion**; a discrete body of material, trapped inside a phenocryst at magmatic temperatures, whether fluid (melt, aqueous solution or vapour) or crystalline at the time of trapping. This term carries no genetic implications.
- **Melt inclusion**; used specifically for inclusions which I can demonstrate trapped a melt phase.
- **Glass inclusion**; a melt inclusion whose content at room temperature are primarily glass, such inclusions usually contain one or more shrinkage bubbles (fig 1) and, more rarely, contain quartz daughter crystals and/or trapped microphenocrysts.
- **CR&GT glass inclusions**; at Okataina most glass inclusions have crystal-rich (fig 2), or granular textures (fig 3). Herein, any glass inclusion other than clear glass inclusions are referred to collectively as crystal-rich and granular-textured (CR&GT) glass inclusions. This distinction is made because there may be differences in homogenisation behaviour between coexisting CR&GT and clear glass inclusions.
- **Crystallised silicate melt inclusions (CSMI's)**; all silicate inclusions (excluding microphenocryst) with completely crystalline texture (fig 4). Characteristically, they contain an interlocking mass of tiny silicate crystals  $\pm$  interstitial aqueous vapour at room temperature. They have a dark, inhomogeneous appearance in transmitted light, but are white in reflected light.
- **Composite inclusions**: melt inclusion that have heterogeneously trapped two or more phases that coexisted in the melt. Consequently, each phase can be found as primary magmatic inclusions in the same samples. Typically, they may contain

silicate melt (now glass), crystallised silicates, globules of aqueous fluid (liquid or vapour), and microphenocrysts (fig 5).

- **Microphenocryst inclusion;** a magmatic inclusion that was already crystalline at the time of trapping; these are commonly found attached to, or enclosed by glass inclusions (fig 6).
- **Fluid inclusion;** inclusions that contain significant amounts of fluid (in this study H<sub>2</sub>O, liquid and/or vapour) at room temperature.
- **Shrinkage bubble;** sensu stricto this refers to a bubble that forms during cooling, as a result of the inclusion shrinking at a greater rate than host. This should produce a bubble that is approximately a vacuum, however, diffusion within the inclusion may introduce significant amounts of volatiles, and immiscible phase droplets may merge with the bubble.
- **Globules;** melt inclusions are described in this study which contain globules of 1- or 2-phase aqueous liquid  $\pm$  crystalline phases. It will be demonstrated that these were co-trapped, or exsolved from the melt post-trapping. In contrast to shrinkage bubbles, which probably contain only low pressure water vapour, globules refer to higher density phases which may represent co-trapped, and therefore immiscible phases.
- **Devitrified inclusion;** used sensu stricto, where there is clear evidence that the inclusion contained a solid glass phase which has subsequently crystallised.

### Contents of inclusion types used in this study

Inclusion type:	Glass	CSMI's	Composite	Fluid	Crystal-rich glass	granular-textured
<b>CONTENTS</b>						
<b>Silicate glass</b>	<b>always</b>	<b>=</b>	<b>always</b>	<b>=</b>	<b>always</b>	<b>always</b>
<b>Shrinkage bubble(s)</b>	<b>always</b>	<b>=</b>	<b>always</b>	<b>=</b>	<b>always</b>	<b>always</b>
<b>Silicate daughter crystals in glass</b>	<b>common</b>	<b>=</b>	<b>common</b>	<b>=</b>	<b>always</b>	<b>common</b>
<b>Crystalline silicate aggregates</b>	<b>=</b>	<b>always</b>	<b>always</b>	<b>rare</b>	<b>=</b>	<b>=</b>
<b>Aqueous fluid</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>always</b>	<b>common</b>	<b>common</b>
<b>Non-silicate daughter crystals</b>	<b>=</b>	<b>common</b>	<b>probable</b>	<b>common</b>	<b>=</b>	<b>common</b>

Glass, CSMI's, and composite inclusions are common to both Río Blanco and Okataina, crystal-rich and granular-textured glass inclusions are found only at Okataina, and fluid inclusions only at Río Blanco.

Figure 1. Clear glass inclusion; containing a small shrinkage bubble in clear rhyolitic glass.

NZL16b. 50µm scalebar

Figure 2. Crystal-rich glass inclusion; containing a large shrinkage bubble and numerous green acicular daughter crystals.

NZL4a. 50µm scalebar

Figure 3. Granular-textured glass inclusion; showing the typical brown, granular appearance. In this example the granular texture results from numerous very small 1- and 2-phase vapour-rich bubbles.

NZL1g. 50µm scalebar

Figure 4. Clear glass inclusion containing trapped zircon and apatite microphenocrysts, a large shrinkage bubble, and green daughter crystals.

NZL27b. 50µm scalebar

Figure 5. A pair of crystalline silicate melt inclusions (CSMI's); showing the characteristic inhomogeneous appearance, and associated decrepitation cracks.

Sample 9903. 50µm scalebar

Figure 6. A composite glass inclusion; containing two clear globules of single-phase aqueous liquid and a large shrinkage bubble, in clear glass. Note the shape of the globules, which suggest plastic deformation, in contrast to the shrinkage bubble, which is almost spherical.

NZL4a. 50µm scalebar

Figure 1



Figure 2



Figure 3



Figure 4

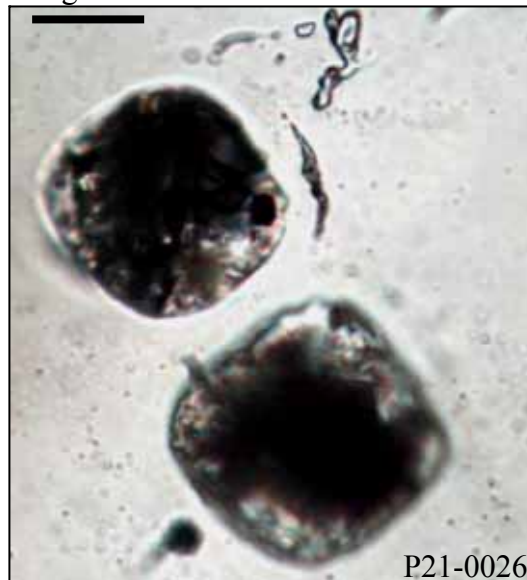


Figure 5



Figure 6







